An Integrated Approach to Utilization of Coal for Specialty Chemicals, Materials and Advanced Jet Fuels

Chunshan Song* and Harold H. Schobert

Applied Catalysis in Energy Laboratory, The Energy Institute, and
Department of Energy & Geo-Environmental Engineering, Pennsylvania State University
209 Academic Projects Building, University Park, PA 16802-5000

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ABSTRACT
This paper will discuss an approach in research for more effective conversion and comprehensive (fuel and non-fuel) utilization of coal for making specialty organic chemicals, carbon-based materials and advanced thermally stable jet fuels. It also discusses shape-selective synthesis of specialty chemicals and polymer materials from coal-derived liquids.

1. INTRODUCTION
This article is a selective overview for recent research in our laboratory that was designed for more effective conversion and comprehensive utilization of coal for making specialty organic chemicals, carbon-based materials and advanced thermally stable jet fuels. We are taking an integrated approach for both non-fuel and fuel uses that make effective uses of the unique structural features of coals. The non-fuel uses of coal has been discussed at length in our previous reviews that were written in response to the invitations by the late Prof. Frank Derbyshire [Song and Schobert, 1993, 1996].

2. SPECIALTY CHEMICALS
Coal-derived liquids contain various 1-ring to 4-ring aromatic structures. Many of the 2-4 ring structures are not readily available from petroleum, and thus the coal tars are still the major sources of the 2- to 4-ring aromatic chemicals in the world today. Our attention on chemicals has focused on shape-selective catalytic synthesis of value-added chemicals from polycyclic aromatic compounds that are rich in coal liquids and some refinery streams. As outlined in recent reviews [Song, 1998, 1999], we are studying ring-shift isomerization of phenanthrene derivatives to anthracene derivatives, shape-selective alkylation of naphthalene, shape-selective alkylation of biphenyl, conformational isomerization of cis-decahydronaphthalene, and shape-selective hydrogenation of naphthalene, and regio-selective hydrogenation of hetero-aromatic compounds, as described below.

Ring-Shift Isomerization. Phenanthrene and its derivatives are rich in various coal-derived liquids such as coal tars, but their industrial use is still very limited. On the other hand, anthracene and its derivatives have found wide industrial applications. We have found that some mordenite and ion-exchanged Y zeolite catalysts selectively promote the transformation of sym-octahydrophenanthrene (sym-OHP) to sym-octahydroanthracene (sym-OHAn), which we call ring-shift isomerization, as shown in Scheme I. The selectivity and activity of the catalysts also depend on the reaction conditions. This reaction is in distinct contrast to the well-known ring-contraction isomerization which results in methylindane-type products.

Scheme I

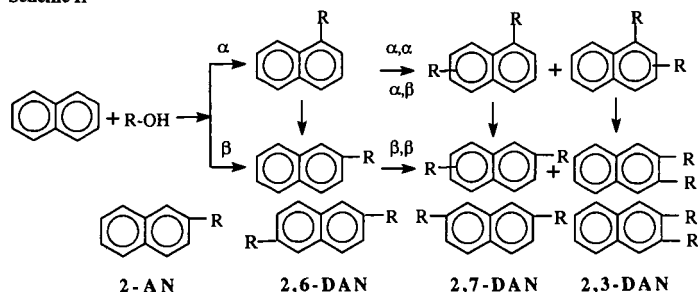**sym-OHP**   **sym-OHAn**

Under mild conditions, some zeolites can afford over 90% selectivity to sym-OHAn with 50% conversion of sym-OHP. This could provide a cheap route to anthracene and its derivatives, which are valuable chemicals in demand, from phenanthrene that is rich in liquids from coal. Possible uses of sym-OHAn include the manufacturing of anthracene (for dyestuffs), anthraquinone (pulping agent), and pyromellitic dianhydride (the monomer for polyimides such as Du Pont's Kapton).

Shape-selective alkylation of naphthalene. Due to the demand for monomers for making the advanced polymer materials such as PEN and PBN, 2,6-dialkyl substituted naphthalene (2,6-DAN) is needed now for making the monomers for PEN, PBN and LCPs. In tars or liquids derived from coal, naphthalene and its derivatives are major components. Shape-selective alkylation over molecular sieve catalysts can produce 2,6-DAN. There are ten possible DAN isomers (Scheme II). The β,β-selective alkylation over molecular sieve catalysts can produce 2-alkylnaphthalene, 2,6-, 2,7-, and 2,3-DAN [Frankel et al., 1986; Komatsu et al., 1994]

The key challenge is to obtain 2,6-DAN with high selectivity, which means increasing the ratio of 2,6/2,7-DAN. Many reports have been published on synthesis of 2,6-DIPN (diisopropylnaphthalene) [Katayama et al., 1991; Moreau et al., 1992] because isopropylation can give much higher selectivity to the 2,6-isomer than the methylation, and an excellent review has been published by Sugi and Kubota [1997]. The results from our laboratory showed that by using partially dealuminated mordenite catalysts, selective alkylation of naphthalene can be achieved with over 65% selectivity to 2,6-DIPN by using isopropanol with 2,6-DIPN/2,7-DIPN ratio of about 3 or using propylene as the alkylating agent with 2,6-DIPN/2,7-DIPN ratio of >2. We also found some simple and effective methods for enhancing the shape selectivity to 2,6-DIPN by using water and chemically dealuminated mordenite.

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* Corresponding author: Email: csong@psu.edu; Fax: 814-865-3248; Tel: 814-863-4466

Scheme II

2-AN   **2,6-DAN**   **2,7-DAN**   **2,3-DAN**

Shape-selective Alkylation of Biphenyl.   Biphenyl and its derivatives are present in coal-derived liquids, although at concentrations lower than those of naphthalene derivatives. Shape-selective alkylation of biphenyl (Scheme III) can produce 4,4'-dialkyl substituted biphenyl (4,4'-DAB), the starting material for monomer of some LCP materials represented by Xydar. Proton-form mordenite can be used as shape-selective catalyst for isopropylation of biphenyl.

Lee et al. [1989] first demonstrated the beneficial effect of dealumination for selective formation of 4,4'- diisopropylbiphenyl (4,4'-DIPB). Sugi and coworkers have carried out a series of studies on biphenyl isopropylation over mordenites [Sugi and Kubota., 1997]. They have reported on the influence of propylene pressure, effects of SiO_2/Al_2O_3 ratio of mordenites, on shape-selectivity and coke deposition, and impact of cerium exchange of sodium mordenite. It was shown in our report that dealumination of some commercial mordenites by acid treatment first increases then decreases their activity, but increases their selectivity toward 4,4'-DIPB in isopropylation with propylene. More recently, we have found that addition of water to dealuminated mordenite is a simple method to inhibit deactivation of the partially dealuminated mordenite catalysts without losing activity and selectivity.

Scheme III

4,4'-DAB   **3,4'-DAB**   **3,3'-DIPB**
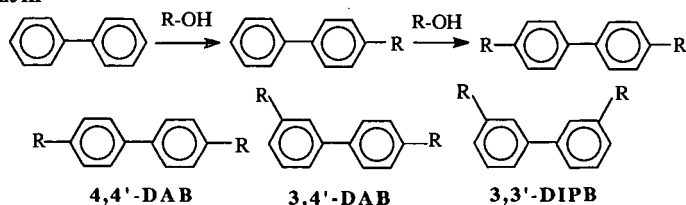
Conformational Isomerization.   Commercial decalins obtained from naphthalene hydrogenation are almost equimolar mixtures of cis-decalin and trans-decalin. In the course of studying sym-OHP isomerization using decalin as solvent, we accidentally found that cis-decalin isomerizes to trans-decalin over ion-exchanged Y zeolite and mordenite catalysts at low temperatures (250°C), as shown in Scheme IV. This reaction would require a temperature of above 400°C in the absence of a catalyst.

Scheme IV

cis-DeHN   trans-DeHN
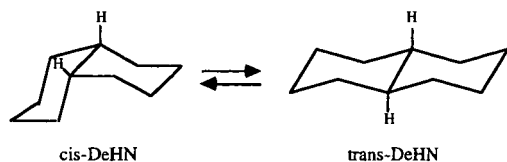
The catalytic reactions were mainly conducted at 200-250 °C for 0.15-8 h under an initial pressure of 0.79 MPa N_2 or H_2 using six catalysts: a hydrogen Y zeolite, a lanthanum ion-exchanged Y zeolite, a hydrogen mordenite, and three noble metal loaded mordenites. Pt- and Pd-loaded mordenites displayed the highest selectivity towards trans-DeHN (nearly 100%), with a trans-DeHN/cis-DeHN ratio of about 13 under H_2 at 200°C; however, they are less effective under N_2. Pre-reduction of Pt/HM30A could improve its catalytic effectiveness in N_2 atmosphere.

By using mordenite-supported platinum or palladium catalysts, it is possible to achieve over 90% conversion with 95% selectivity at 200°C. trans-Decalin has substantially higher thermal stability at temperatures above 400°C. Possible applications of this process are high-temperature heat-transfer fluids and advanced thermally stable jet fuels, which can be used both as heat sinks and as fuels for high-Mach aircraft.

Shape-Selective Hydrogenation of Naphthalene.   Complete   hydrogenation   of naphthalene in conventional processes produces mixtures of cis- and trans-decalin. Our work on selective naphthalene hydrogenation is motivated from the accidental finding on zeolite-catalyzed isomerization of cis-decalin and from the need to tailor the formation of desired isomers from two-ring compounds. Our previous studies on naphthalene hydrogenation showed that certain catalysts

show higher selectivity towards cis-decalin or trans-decalin. More recently, we found that mordenite and Y zeolite-supported Pt and Pd catalysts can selectively promote the formation of cis-decalin or trans-decalin, as shown in Scheme V.

Scheme V
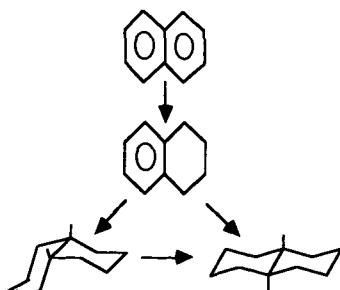
Now we can produce cis-decalin, with over 80% selectivity (or over 80% trans-decalin) at 100% conversion by using some zeolite-supported catalysts at 200°C. cis-Decalin may have potential industrial application as the starting material for making sebacic acid. Sebacic acid can be used for manufacturing Nylon 6,10 and softeners. There is also an industrial need for selective production of tetralin, a hydrogen-donor solvent, from naphthalene. Partial passivation of some zeolite-supported noble metal catalysts by sulfur can make them highly selective for the production of tetralin during metal-catalyzed hydrogenation of naphthalene at low temperatures.

Regio-Selective Hydrogenation. More recently we have begun to explore regio-selective hydrogenation of heteroatom-containing aromatic compounds. Examples of such compounds are 1-naphthol and quinoline shown in Scheme VI. Partial hydrogenation of 1-naphthol can give 1,2,3,4-tetrahydro-1-naphthol (THNol-1) and 5,6,7,8-tetrahydro-1-naphthol (THNol-2). Under fuel hydrotreating conditions, hydrogenolysis of C-O bond can also take place. It is of interest to see whether we can selectively produce THNol-1. We are conducting experimental work on regio-selective hydrogenation over various metal catalysts supported on zeolites, alumina and titania. As in the case of naphthalene hydrogenation described above, the type of metal and support were found to be important for achieving regio-selectivity (for example, to THNol-1) (Shao et al., 2000). Similarly, for partial hydrogenation of quinoline, either 1,2,3,4-tetrahydroquionoline (THQ-1) or 5,6,7,8-tetrahydroquionoline (THQ-2) can be produced. It is interesting to clarify how can one of the two isomers be produced selectively under practically useful conditions for catalytic processing. The hydroaromatic products of regio-selective hydrogenation have some unique applications, e.g. as hydrogen donors or radical scavengers for stabilizing fuels at high temperatures [Andresen et al., 1999; Venkatraman et al., 1998].

Scheme VI

THNol-1   THNol-2

THQ-1   THQ-2
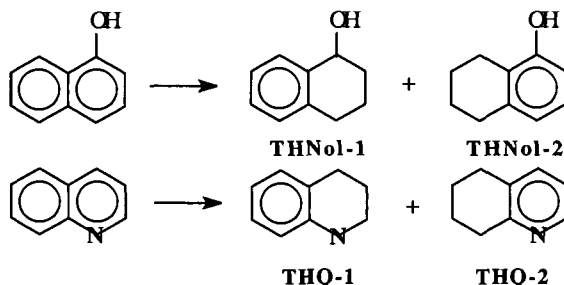
3. CARBON MATERIALS
Since all coals are carbon-rich solids, they are potential starting materials for other, higher value materials via conversion to new carbon-based solids. It is now well known that various useful carbon-based materials and composite materials can be made from coals, coal tars, petroleum pitch, and coal liquids from liquefaction and coal pyrolysis, as shown in Table 1 [Song and Schobert, 1993].

Table 1. List of Some Coal-Based Carbon Materials

Materials That Can be Made Using Coal	Materials from Coal-derived Liquids
Metallurgical coke	Pitch-based carbon fibers
Activated carbon adsorbents	Mesocarbon microbeads
Molecular sieving carbons	Carbon Electrodes
Graphite and graphite-based materials	Binder pitches
Composite (coal/polymer) materials	Activated carbon fibers
Fullerenes or "bucky-balls"	Mesophase-based carbon fibers
Carbon nano tubes	Carbon whiskers or filament
Diamond-like films	Carbon fiber reinforced plastic
Intercalation Materials	Carbon-based Honeycomb

Production of activated carbons from coals has been of interest for years. Excellent reviews, with abundant historical information, has been published by Derbyshire and colleagues [Derbyshire et al., 1995; Derbyshire, 1998]. Activated carbons are used mainly as adsorbents for liquid- and gas-phase applications. The amount of coals used worldwide for producing activated carbons is about 200,000 t/y [Golden, 1992], a significant fraction of the world's annual production of activated carbons, estimated to be about 450,000 t from all feedstocks. Significant growth potential exists for this application, primarily for water and air purification. The liquid-phase applications of activated carbons produced from bituminous coals by chemical activation include water purification, decolorizing, food processing, and gold recovery; the gas-phase applications cover air purification, gas treatment, and solvent recovery [Jagtoyen et al., 1993]. Activated anthracites produced by air treatment prior to steam activation are microporous with a significant fraction of the pores having molecular dimensions [Gergova et al., 1995]. This suggests that molecular sieve materials could be produced from anthracites.

Current graphite technology uses petroleum cokes as the filler material. Molded graphite articles have a wide range of applications, from high-tonnage uses as electrodes in electric arc furnaces, a \$US2.2 billion business in 1991 [Pierson, 1993], to specialty graphites for high-technology uses in chemical vapor deposition and epitaxial deposition devices. Meta-anthracite, of very limited value (≈$US25/ton) because of its poor combustion performance, may be a superior filler for molded graphites, even better than the more conventional anthracites. For example, non-catalytic graphitization of meta-anthracite at 2400°C yields a product having a 0.3363 nm d-spacing [Morrison et al., 1996], compared with the 0.335 nm value of pure graphite. The value of meta-anthracite as a replacement for petroleum coke in graphite production would exceed its value as a fuel by about a factor of ten.

The amount of coals used worldwide for producing molecular sieving carbons (MSC) is estimated to be 3,000 tonnes/year [Golden, 1992]. The application MSC for gas separation by pressure-swing adsorption is now commercially viable. In the United States, MSC is used for air separation by Air Products and Chemicals Inc. It is likely that more companies will be engaged in producing MSC in the next century.

Coal tar pitches are raw materials for carbon fibers and mesocarbon microbeads [Derbyshire et al., 1994]. Liquids from coal extraction and liquefaction can be used for making carbon fibers and graphitic materials [e.g., Zondlo et al., 1993]. Kimber and Gray [1976] also noted potential advantages in using coal-based coke for making carbon electrodes.

4. ADVANCED JET FUELS

One commercially available route to make liquid fuels from coal is the well-known SASOL route incorporating coal gasification as the first step and the Fischer-Tropsch synthesis as the second step. The fuels from Fischer-Tropsch synthesis using either natural gas- or coal-derived syngas are good as diesel fuels. However, for jet fuel applications, there is an unique structural advantage of coal that can lead to superior fuels. There are some unique compositional advantages of coal-derived liquids for making jet fuels, with respect to the high-temperature thermal stability required for future supersonic and hypersonic jet aircraft. The USAF has established a long-term goal to develop advanced jet fuels called JP-900 that are stable at high temperatures up to 900 °F (482 °C) [Edwards et al., 1997].
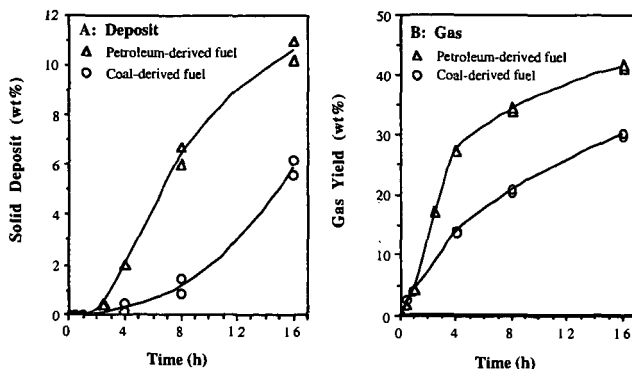
Figure 1. Formation of solid deposit (A) and gases (B) from petroleum-derived JP-8P and coal-derived JP-8C jet fuels at 450°C for 0.5-16 h under nitrogen atmosphere (100 psi, cold).

As can be seen from Figure 1, compared to conventional petroleum derived jet fuels, the coal-derived jet fuels display greater thermal stability at temperatures above 400 °C in the pyrolytic regime, in terms of much lower degree of decomposition and significantly less amount of solid deposit [Lai et al., 1992; Song et al., 1993]. This is because coal-derived jet fuels are rich in cycloalkane and the aromatic compounds in coal-derived jet fuels can be dominated by hydroaromatic structures. Cycloalkanes are more stable than the n-alkanes with the same or less carbon number, and the stability of alkylated cycloalkanes decreases with increasing length or carbon number of the side chain [Lai and Song, 1996; Song and Lai, 1998]. At temperatures above 400°C, decomposition of long-chain paraffins in jet fuels is dominated by radical-chain reactions [Song et al., 1994a]. Hydroaromatic compounds such as tetralin are hydrogen donors which can serve as radical

scavengers in pyrolytic reactions which inhibit the thermal decomposition of reactive hydrocarbons [Song et al., 1994b; Yoon et al., 1996]. Studies on model paraffinic jet fuels in the absence and the presence of added hydroaromatic compounds have also demonstrated that they are capable of suppressing the initial decomposition by retarding the radical reactions [Venkatraman et al., 1998; Andresen et al., 1999].

Coal-derived JP-8C fuel and a model jet fuel that contains mainly cycloalkanes and about 10% tetralin has been shown to be thermally stable at temperatures up to 482°C or 900 °F [Strohm et al., 1999].

The coal-based thermally stable jet fuels can be produced using liquids that are partially or wholly derived from coal, by one of the following strategies: (1) the use of by-product coal tars from coal carbonization or from coal gasification (pyrolysis); (2) the use of blends of coal tar distillates and petroleum refinery streams, which would enlarge the pool of available feedstock; (3) the use of by-product liquids from co-coking of coal and petroleum resids; and (4) the use of liquids from co-processing of coal and petroleum resids, which is a process alternative to the well-known direct liquefaction of coal.

5. CONCLUDING REMARKS
We must always keep in mind that coal is a valuable hydrocarbon source, that can have multiple and equally important uses for both non-fuel and fuel applications. As we move into the 21st century, coal may become more important both as an energy source and as the source of chemical feedstocks.

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